

1 **METHOD OF PRODUCING QUANTUM-DOT POWDER AND FILM VIA**
6 **TEMPLATING BY A 2-D ORDERED ARRAY OF AIR BUBBLES IN A POLYMER**

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6 National Science Foundation. The U.S. government has certain rights on this invention.

BACKGROUND OF INVENTION

(1) Field of Invention

11 The present invention relates to a method for producing nanometer-sized solid particles
and composite film materials containing these nano particles. More particularly, it relates to a
method for producing nanometer-sized particles (diameter smaller than 100 nm or 1,000 Å,
preferably smaller than 50 nm, and most preferably smaller than 20 nm) at a high production rate
using interstitial solution synthesis in a micro-porous or nano-porous material template. In
particular, the present invention is directed to a method of producing such materials with which
16 the formation of the meso-porous or macro-porous polymer film template is accomplished by a
novel self-assembly mechanism of moisture condensation-induced bubble formation.

(2) Description of Prior Art

21 Nanometer-sized semiconductor crystals are of technological significance due to their
unique physical properties such as size quantization, non-linear optic behaviors, and unusual
luminescence. Nanometer-sized semiconductor crystals (or crystallites) or "quantum dots"
whose diameter is smaller than the bulk exciton Bohr diameter (up to 20 nm, but normally
smaller than 10 nm in diameter) represent a class of materials intermediate between molecular
and bulk forms of matter. Quantum confinement of both the electron and hole in all three
26 dimensions leads to an increase in the effective band gap of the semiconductor material with
decreasing crystallite size. As a result, both the optical absorption and emission of quantum dots
shift to the higher energies (blue shift) as the size of the dots gets smaller. Nanometer-sized
semiconductor crystallites that show such a quantum size effect are also referred to as quantum-
sized crystals or quantum nano crystals. Among these, most notable are I-VII, II-VI, III-V, III-VI

1 and IV-VI compound semiconductors.

Quantum-sized compound semiconductors have been found to provide an electro-luminescent device capable of emitting light of various visible wavelengths in response to external stimulus. In such an electro-luminescent device, variations in voltage could result in change of color of the light emitted by the device. Since these classes of light emitting materials are inorganic materials, they are capable of withstanding higher temperatures than the conventional organic polymeric materials for light-emitting applications.

Fluorescent labeling of biological systems is a well known analytical tool used in modern biotechnology as well as analytical chemistry. Applications for such fluorescent labeling include technologies such as medical fluorescence microscopy, histology, flow cytometry, fluorescence in-situ hybridization for medical assays and research, DNA sequencing, immuno-assays, binding assays, separation, etc. Quantum-sized semiconductor crystals have been found to provide stable probe materials for biological applications having a wide absorption band. These crystals are capable of exhibiting either a detectable change in absorption or of emitting radiation in a narrow wavelength band, without the presence of the large red emission tails characteristic of dye molecules. This feature makes it possible to permit the simultaneous use of a number of such probe materials, each emitting light of a different narrow wavelength band and/or being capable of scattering or diffracting radiation. These stable probe materials can be used to image the same sample by both light and electron microscopy.

In addition, compound semiconductor materials comprised of metals and Group 16 elements (commonly referred to as Group VIA chalcogens) are important candidate materials for photovoltaic applications (solar cells), since many of these compounds or metal chalcogenides have optical band gap values well within the terrestrial solar spectra. Mixed-metal chalcogenide semiconductors, such as copper-indium-diselenide (CuInSe_2), copper-gallium-diselenide (CuGaSe_2), and copper-indium-gallium-diselenide ($\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$), all of which are sometimes generically referred to as Cu(In,Ga)Se_2 are of particular interest for photovoltaic device applications because of their high solar energy to electrical energy conversion efficiencies.

1 Sulphur (S) can also be substituted for selenium, so the compound is sometimes also referred to
even more generically as Cu(In,Ga)(Se,S)₂ to comprise all of those possible combinations.

The following patents are believed to represent the state of the art of the manufacturing
methods for semiconductor quantum particles:

1. S. Weiss, et al., "Semiconductor nanocrystal probes for biological applications and process for making and using such probes," U.S. Pat. No. 6,207,392 (March 27, 2001).
2. A. P. Alivisatos, et al., "Process for forming shaped group II-VI semiconductor nanocrystals, and product formed using process," U.S. Pat. No. 6,225,198 (May 1, 2001).
3. A. P. Alivisatos, et al., "Preparation of III-V semiconductor Nanocrystals," U.S. Pat. No. 5,505,928 (April 9, 1996).
4. A. P. Alivisatos, et al., "Electroluminescent devices formed using semiconductor nanocrystals and an electron transport media and method of making such electroluminescent devices," U.S. Pat. No. 5,537,000 (July 16, 1996).
5. S. Weiss, et al., "Organic luminiscent semiconductor nanocrystal probes for biological applications and process for making and using such probes," U.S. Pat. No. 5,990,479 (Nov. 23, 1999).
6. A. P. Alivisatos, et al., "Semiconductor nanocrystals covalently bound to solid inorganic surfaces using self-assembled monolayers," U.S. Pat. No. 5,751,018 (May 12, 1998).
7. M. G. Bawendi, et al., "Water-soluble fluorescent nanocrystals," U.S. Pat. No. 6,251,303 (June 26, 2001).
8. M. G. Bawendi, et al., "Highly luminescent color-selective materials and method of making thereof," U.S. Pat. No. 6,207,229 (March 27, 2001).
9. N. M. Lawandy, "Semiconductor nanocrystal display materials and display apparatus employing same," U.S. Pat. 5,882,779 (March 16, 1999).
10. A. L. Huston, "Glass matrix doped with activated luminiscent nanocrystalline particles," U.S. Pat. No. 5,585,640 (Dec. 17, 1996).
11. H. F. Gray, et al. "Nanoparticle phosphors manufactured using the bicontinuous cubic phase process," U.S. Pat. No. 6,090,200 (July 18, 2000).
12. J. Yang, "Formation of nanocrystalline semiconductor particles within a bicontinuous cubic phase," U.S. Pat. No. 6,106,609 (Aug. 22, 2000).
13. S. L. Castro, et al., "Functionalized nanocrystals and their use in detection systems," U.S. Pat. No. 6,114,038 (Sep. 5, 2000).
14. E. Barbera-Guillem, "Lipophilic, functionalized nanocrystals and their use for fluorescence labeling of membranes," U.S. Pat. 6,194,213 (Feb. 27, 2001).
15. D. Gallagher, et al., "Method of manufacturing encapsulated doped particles," U.S. Pat. No. 5,525,377 (June 11, 1996).
16. C. Lawton, "Biomolecular synthesis of quantum dot composites," U.S. Pat. No. 5,985,353 (Nov. 16, 1999).
17. O. Siiman, et al., "Semiconductor nanoparticles for analysis of blood cell populations and method of making same," U.S. Pat. 6,235,540 (May 22, 2001).
18. J. C. Linehan, et al. "Process of forming compounds using reverse micelle for reverse

- microemulsion systems," U.S. Pat. 5,770,172 (June 23, 1998).
19. C. B. Murray, et al. "Method for producing nanoparticles of transition metals," U.S. Pat. No. 6,262,129 (July 17, 2001).
20. A. N. Goldstein, "Narrow size distribution silicon and germanium nanocrystals," U.S. Pat. No. 6,268,041 (July 31, 2001); No. 5,491,114; No. 5,576,248; No. 5,559,057.
21. E. Barbera-Guillem, "Continuous flow process for production of semiconductor nanocrystals," U.S. Pat. 6,179,912 (Jan. 30, 2001).
22. D. L. Schulz, et al., "Solution synthesis of mixed-metal chalcogenide nanoparticles and spray deposition of precursor films," U.S. Pat. No. 6,126,740 (Oct.3, 2000).
23. P. J. Dobson, et al., "Method of producing metal quantum dot," U.S. Pat.5,965,212 (Oct. 12, 1999).
24. R. L. Wells, et al., "Method of synthesizing III-V semiconductor nanocrystals," U.S. Pat. No. 5,474,591 (Dec. 12, 1995).
25. D. J. Norris, et al., "Three-dimensionally patterned materials and methods for manufacturing same using nanocrystals," U.S. Pat. No. 6,139,626 (Oct.31, 2000).

Bawendi and co-workers have described a method of preparing mono-disperse semiconductor nano crystallites by pyrolysis of organometallic reagents injected into a hot coordinating solvent [Ref.8]. This permits temporally discrete nucleation and results in the controlled growth of macroscopic quantities of nanocrystallites. Size selective precipitation of the crystallites from the growth solution provides crystallites with narrow size distributions. The narrow size distribution of the quantum dots allows the possibility of light emission in very narrow spectral widths. Although semiconductor nanocrystallites prepared as described by Bawendi and co-workers exhibit near monodispersity, and hence, high color selectivity, the luminescence properties of the crystallites are poor. Such crystallites exhibit low photoluminescent yield, i.e. the light emitted upon irradiation is of low intensity. This is due to energy levels at the surface of the crystallite which lie within the energetically forbidden gap of the bulk interior. These surface energy states act as traps for electrons and holes which degrade the luminescence properties of the material.

Since mid-1980's, various synthetic approaches have been developed in preparing nano-sized II-VI (Zn and Cd chalcogenides) and IV-VI (Pb chalcogenides) semiconductors. Much of this effort has been aimed at achieving a very narrow particle size distribution. The basic idea is to use the spatial or chemical confinement provided by matrices or organic capping molecules to terminate the growth of nanocrystallites at any desired stage. In most cases, lack of a

1 microscopically uniform environment in the substrates might be the cause for relatively wide size
distribution. Both organic and inorganic matrices, such as mono-layers, polymers, inverse
micelles, and zeolites have been used to control the particle size. Recently, other researchers
have obtained mono-dispersed CdSe nano crystallites based on the pyrolysis of organometallic
reagents. This approach makes use of the concept of Ostwald ripening for size selective
6 precipitation of nano crystallites. So far, many efforts have been made to synthesize
quantum-sized II-VI semiconductors especially on the $\text{CdS}_x\text{Se}_{1-x}$ systems, while much fewer
efforts on IV-VI (PbX , $\text{X} = \text{S}, \text{Se}, \text{Te}$) compounds have been reported. The IV-VI group of
compound semiconductors exhibits smaller band gaps, greater quantum-size effect and larger
optical non-linearity compared to II-VI materials.

11 Conventional wet chemistry synthesis conducted without matrix assistance tends to result
in the production of micron size particles. Various host matrices, such as glass, zeolites, sol-gels,
and micelles, have been used to synthesize nano particles. However, a number of problems have
been found to be associated with these methods. For instance, the particles synthesized in glasses
and sol-gels exhibit large polydispersity, since they are not ordered structures. Another
16 disadvantage with these methods is the inability to easily isolate the nano particles from the
matrix material. In the case of micelles, even though it is possible to isolate the particles, the low
precursor concentrations required will make mass production of nano particles expensive or
impractical.

21 Compound semiconductor nano crystals, such as Group II-VI ones, may be formed by
dissolving a Group II precursor and a Group VI precursor in a solvent and then applying heat to
the resulting solution. For example, Group II-VI semiconductor nano crystals may be formed by
dissolving a dialkyl of the Group II metal and a Group VI powder in a trialkyl phosphine solvent
at ambient temperature, and then injecting the mixture into a heated ($340^\circ\text{--}360^\circ\text{C}$) bath of
26 tri-octyl phosphine oxide (TOPO). While this process is capable of producing Group II-VI
semiconductor nano crystals, the results can be somewhat erratic in terms of average particle size
and size distribution. This problem of not being reproducible is likely due to the impurities in the
technical grade (90% pure) TOPO that adversely influence the reaction. However, substitution

1 of pure TOPO for the technical grade TOPO has also been unsatisfactory, particularly when
control of the shape of the particle growth is also desired, clearly because the pure TOPO binds
too weakly to the growing crystallites and only weakly associates with the Group II metal to act
as a growth retardant, resulting in the growth of spheres rather than any other desired shapes. It
seems that the presence of impurities in the technical grade TOPO results in the erratic success of
6 Group II-VI semiconductor nanocrystal growth in technical grade TOPO.

Alivisatos et al. [Ref.3] describes a process for forming Group III-V semiconductor nano
crystals wherein size control is achieved through use of a crystallite growth terminator which
controls the size of the growing crystals. Crystallite growth terminators are said to include a
11 nitrogen-containing or a phosphorus-containing polar organic solvent having an unshared pair of
electrons. The patent further states that this growth terminator can complex with the metal and
bind to it, thereby presenting a surface which will prevent further crystal growth.

Schulz, et al. [Ref.22] discloses a solution synthesis method for producing mixed-metal
chalcogenide nano particles. Wells, et al. [Ref.24] describes a method of synthesizing III-V
16 semiconductor nano crystals in solution at a low temperature. Barbera-Guillem, et al. teaches a
five-step, continuous flow process for production of semiconductor nano crystals.

All of these techniques have one or more of the following problems or shortcomings:

- 21 (1) Most of these prior-art techniques suffer from a severe drawback: extremely low
production rates. These low production rates, resulting in high product costs, have
severely limited the utility value of nano crystals. There is, therefore, a clear need for a
faster, more cost-effective method for preparing nanometer-sized semiconductor
materials.
- 26 (2) Most of the prior-art techniques tend to produce a compound nano crystal product which
is constituted of a broad particle size distribution.
- (3) Most of the prior-art processes require heavy and/or expensive equipment, resulting in
high production costs.

1 The present invention is directed to a method of producing quantum-dot solids (including
quantum dot powder and solid films) using a novel porous polymer-templating approach. Porous
solids of both natural and synthetic design have been utilized in a wide range of applications,
including membranes, catalysts, energy storage, photonic crystals, microelectronic device
substrate, absorbents, light-weight structural materials, and thermal, acoustical and electrical
6 insulators. The pore structures of such solids are generally formed during crystallization or
during subsequent treatments. These solid materials are classified depending upon their
predominant pore sizes: (i) micro-porous solids, with pore sizes <1.0 nm; (ii) macro-porous
solids, with pore sizes exceeding 50 nm (normally up to 500 μm); and (iii) meso-porous solids,
with pore sizes intermediate between 1.0 and 50 nm. The term "nano-porous solid" means a
11 solid that contains essentially nanometer-scaled pores (1-1,000 nm) and, therefore, covers "meso-
porous solids" and the lower-end of "macro-porous solids". For quantum-dot powder
applications, the subject invention concerns primarily with semiconductor particles smaller than
20 nm in diameter and the solid composite films containing these particles.

16 Norris, et al. [Ref.25] proposed a method of producing a 3-D quantum-dot solid that also
involves the utilization of a reticulated template. The method entails filling the pores in a
template with colloidal nanocrystals. The quantum-dot solid is formed when the colloidal
nanocrystals are concentrated as close-packed nanocrystals within the pores of a 3-D template.
The work of Norris, et al. was limited to the formation of bulk 3-D patterned materials, not thin-
21 film composite or quantum particles. Furthermore, it made use of pre-fabricated colloidal
nanocrystals to fill in the pores of a pre-fabricated 3-D network of pores. Norris, et al. failed to
fairly suggest how a 2-D or 3-D network of pores might be best prepared, fast and cost-
effectively, for use as a reticulated template.

26 Accordingly, one object of the present invention is to provide an improved method for
producing quantum-size semiconductor particles and a thin composite film containing these
particles.

Another object of the present invention is to provide a method that is capable of
producing a wide range of quantum-size semiconductor materials at a high production rate.

1 A further object of the present invention is to provide a method that is capable of
producing quantum-size semiconductor materials, both powders and films, by using a nano-
porous polymer film templating approach.

SUMMARY OF THE INVENTION

6 One embodiment of the present invention is a method for producing a quantum-sized
material according to a predetermined, two-dimensional nano-porous polymer template. The
method includes the steps of: (a) preparing a nano-porous polymer or organic template, wherein
the preparation step includes the sub-steps of (i) dissolving a polymer in a volatile solvent to
form an evaporative solution, (ii) depositing a thin film of this solution onto a substrate, and (iii)
11 directing a moisture-containing gas to flow over the spread-up solution film while allowing the
solvent in the solution to evaporate for forming a template, which is constituted of an ordered
array of nanometer-scaled air bubbles with polymeric walls dispersed in a polymer film; (b)
filling the air bubbles with a precursor fluid; and (c) converting the precursor fluid in such
bubbles to obtain a quantum-sized material in the form of an array of dots supported in the
16 template. At least one of the dot dimensions is on the 100 nm scale or smaller, preferably
smaller than 20 nm.

The method may include an additional step of removing the polymeric walls to recover
the quantum-sized material in a powder form. The method may further include a step of re-
melting and re-solidifying the polymeric walls to consolidate the polymer film. The quantum-
sized material may be a material selected from the group consisting of (i) group I-VII
semiconductors, (ii) group II-VI semiconductors, (iii) group III-V semiconductors, (iv) group IV
semiconductors, (v) metals, or (vi) metal oxides. The group I-VII semiconductors are preferably
selected from the group consisting of CuCl, AgBr, and NaCl. The group II-VI semiconductors
are preferably selected from the group consisting of ZnO, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe,
26 HgS, HgSe, HgTe, and alloys of these materials. The group III-V semiconductors are selected
preferably from the group consisting of GaP, GaAs, InP, InAs, InSn, and alloys of these
materials. The group IV semiconductors are preferably selected from the group consisting of C,
Si, Ge, and alloys of these materials. The metals are preferably selected from the group

consisting of Ni, Cu, Ag, Pt, and Au. The metal oxides are preferably selected from the group consisting of silica, titania, alumina, and zirconia.

The method may further include a step of (d) removing the polymeric walls, such that a plurality of voids are formed in the quantum-sized material in positions which were occupied by the polymeric walls prior to the removal of the polymeric walls, wherein the quantum-sized material is self-supporting. The removal of polymer walls may be accomplished by immersing the template in a polymeric wall-selective etchant or solvent. The method may further include the step of (e) refilling the voids with a supporting material. The supporting material preferably has an index of refraction that is lower than that of the quantum dots.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG.1 A flowchart showing the essential steps of a method for producing quantum-sized semiconductor material in accordance with a preferred embodiment of the present invention.

FIG.2 A micrograph showing an ordered array of bubbles with polymer walls.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

A preferred embodiment of the present invention is a method for producing a quantum-sized material according to a predetermined, two-dimensional nano-porous polymer template.

The first step of this method involves the preparation of a nano-porous polymer template. This step includes several sub-steps (FIG.1):

- (i) dissolving a polymer **12** in a volatile solvent **14** to form an evaporative solution **16**,
- (ii) depositing a thin film of this solution onto a substrate **18** (e.g., the surface of a boro-silicate glass or silicon plate), and
- (iii) exposing the solution film **20** on the substrate to a moisture environment (e.g., by directing a moisture-containing gas to flow over this solution film) while, concurrently and/or subsequently, allowing the solvent in this solution to rapidly evaporate for forming a template **22**. The template is constituted of an ordered array of nanometer-scaled air bubbles with polymeric walls dispersed in a polymer film. It is believed that rapid vaporization of the solvent induces a temperature

1 reduction in the vicinity of the solution film. This low temperature environment is conducive to
the formation of water droplets or “dew” near the solution-vapor interface. These water droplets,
micrometer- or nanometer-scaled, try to sink through the film made of an organic material
(preferably a polymer or an oligomer, which is a low molecular mass polymer). This polymer
makes up the walls of the water droplet. Water molecules eventually leave the film, leaving
6 behind “air bubbles” or voids in the film template. Hence, the template is constituted of an
ordered array of micrometer- or nanometer-scaled “air bubbles” with polymeric walls dispersed
in a polymer film (e.g., FIG.2).

11 The preparation of a nano-porous polymer template is similar to the procedures used by
M. Srinivasarao, et al. (Science, vol.292, 6 April 2001, pp.79-83), G. Widawski, et al. (Nature,
vol.369, 2 June 1994, pp.387-389), and O. Pitois and B. François (Eur. Physical Journal, B8,
1999, pp.225-231). The polymers that can be used in practicing the present patent includes
simple coil type polymers (e.g., linear polystyrene), star-shaped polymers (e.g., star-polystyrene),
and rod-coil copolymers (e.g., polyparaphenylene-polystyrene block copolymer). A wide range
16 of solvents can be used to dissolve these polymers, including benzene, toluene, and carbon
disulfide (CS₂).

21 A thin layer of the prepared solution is deposited onto a flat substrate, e.g., via spraying.
The solvent in this thin layer of solution is allowed to rapidly evaporate in the presence of
moisture. The procedure may be accelerated by sending a flow of moisture-containing nitrogen
gas across the surface of this thin solution layer. In a matter of seconds, the solvent evaporates,
leaving behind an ordered array of holes or air bubbles on the solid polymer film surface. These
typically spherical holes are organized in a compact hexagonal network with micro-porous
polymeric walls separating these spherical holes. We have found that, by manipulating the
26 temperature, moisture level, and gas flow rate, one can vary the pore sizes in a controlled fashion.
Although Srinivasarao, G. Widawski, O. Pitois, and their respective co-workers have observed
that the pore sizes are within the range of 0.20 to 20 μm , we have found that uniformly-sized
nano pores with a pore size in the range of 1 - 100 nm are readily obtainable.

The subsequent steps of the method include filling the air bubbles in the nano-porous template with a precursor fluid and converting the precursor fluid in the bubbles to obtain a quantum-sized material. The resulting material is in the form of an array of dots supported in the template. At least one of the dot dimensions is on the 100 nm scale or smaller, and most preferably 20 nm or smaller. The quantum-sized material can be a metal, a single-component semiconductor (e.g., C, Si, Ge), a compound semiconductor (composed of a "metal element" for forming a cation and a non-metal "reactant element" such as O, S, Se, and Te for forming an anion), or an oxide.

As used herein, the term "metal element" in a compound semiconductor refers to an element of Groups 2 through 13, inclusive, plus selected elements in Groups 14 and 15 of the periodic table. Thus, the term "metal element" broadly refers to the following elements:

Group 2 or IIA: beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra).

Groups 3-12: transition metals (Groups IIIB, IVB, VB, VIB, VIIB, VIII, IB, and IIB), including scandium (Sc), yttrium (Y), titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), niobium (Nb), tantalum (Ta), chromium (Cr), molybdenum (Mo), tungsten (W), manganese (Mn), technetium (Tc), rhenium (Re), iron (Fe), ruthenium (Ru), osmium (Os), cobalt (Co), rhodium (Rh), iridium (Ir), nickel (Ni), palladium (Pd), platinum (Pt), copper (Cu), silver (Ag), gold (Au), zinc (Zn), cadmium (Cd), and mercury (Hg).

Group 13 or IIIA: boron (B), aluminum (Al), gallium (Ga), indium (In), and thallium (Tl).

Lanthanides: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu).

Group 14 or IVA: germanium (Ge), tin (Sn), and lead (Pb).

Group 15 or VA: antimony (Sb) and bismuth (Bi).

However, in a preferred embodiment, the metal element is selected from Groups IB (Cu, Ag, and

1 Au), IIB (Zn, Cd, and Hg), IIIA (Al, Ga, In, and Tl), IVA (Ge, Sn, and Pb), and VA (Sb and Bi)
for luminescence applications. In another preferred embodiment, the metal element is selected
from the group consisting of copper, indium, gallium, or cadmium for photovoltaic device
applications.

6 As used herein, the "reactant element" used in a precursor fluid is an element selected
from Group 15 (or Group VA, including phosphorus (P) and arsenic (As)) or Group 16 (or Group
VIA, including oxygen (O), sulfur (S), selenium (Se), and tellurium (Te)). The term "chalcogen"
normally refers to an element of Group 16 of the periodic table (including S, Se, and Te). The
term "chalcogenide" normally refers to a binary or multinary compound containing at least one
11 chalcogen and at least one more electropositive element or radical (e.g., from one of the metal
elements defined earlier). Preferably, the chalcogen is sulfur, selenium, or tellurium, and the
"metal chalcogenide" is preferably a metal sulfide, a metal selenide, a metal telluride, or some
mixture thereof. For the purposes of specification and claims herein, however, the term
"chalcogen" refers to an element selected from the group consisting of P, As, S, Se, and Te) and
16 the term "metal chalcogenide" includes a metal phosphide, a metal arsenide, a metal sulfide, a
metal selenide, a metal telluride, or some mixture thereof, unless otherwise indicated.

The "precursor fluid" composition used herein may be a "metal salt". The "metal salt"
used in the methods of the present invention may be any compound which contains a metal, and
whose sodium salt (e.g., NaX) is soluble in the organic solvent used to precipitate the metal
21 chalcogenide. When used in the context of a metal salt, the term "salt" refers to halogenides,
sulfates, nitrates, phosphates, complex salts, alcoholates, phenolates, carbonates, carboxylates,
metallo-organic compounds, and the like. Preferably, the salt is a halogenide (e.g., NaI) or a
metallo-organic compound.

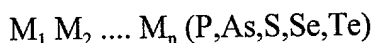
26 This invention provides a method of producing compound semiconductor nano particles,
including metal phosphide, metal arsenide, and metal chalcogenide nano particles by using a
solution synthesis process. The metal phosphide, arsenide, and chalcogenide nano particles are
preferably passivated with a capping agent or protective coating. The development of nano

1 crystals in a solution synthesis process typically involves three distinct phases: nucleation (initial
formation of particle nuclei, which are nanometer-scaled clusters of atoms, ions, and/or
molecules), crystal growth (addition of metal cation and anion to the growing faces of crystal
lattices of particle nuclei rather than being consumed in the formation of new particle nuclei),
and termination of crystal growth. The method according to the present invention is directed to
6 precisely manipulating parameters for controlling the crystallization processes involved in
production of semiconductor nano crystals.

11 In one embodiment of the present invention, referring to FIG.1 (after the template 22 is
prepared), the method further includes a step of providing a metal-containing precursor 2 and a
reactant-containing precursor 4 and allowing these two precursors to mix and react in a
mixing/reacting chamber 6 to form a reacting fluid or a precursor fluid. This precursor fluid is
introduced into the nano pores in the template to form a filled template 24. The reacting fluid is
allowed to undergo a chemical reaction or phase transformation in such a fashion that
nanocrystals are formed in the pores, separated by thin walls in a polymer template 26. For
16 instance, this step may involve reacting a metal salt with a chalcogenide salt (or phosphide or
arsenide salt) in an organic solvent to precipitate nano-size clusters of a compound
semiconductor (e.g., a metal chalcogenide, phosphide, or arsenide) out of a solution trapped in
the nano pores of the nano-porous polymer template. The pore walls serve to constrain or
terminate the growth of these nano clusters, which cannot grow larger than the pore sizes that are
21 nanometer-scaled. Optionally, the solution may be made to contain a volatile
capping/passivating agent to cap, passivate or protect the nano clusters) to produce stabilized
(separated and/or passivated) nano particles.

26 As indicated earlier, for the purpose of providing a detailed description and an enabling
embodiment, but not for the purpose of limitation, this description hereinafter uses the term
"metal chalcogenides" to include metal pnictides (phosphides and arsenides) and conventional
metal chalcogenides (sulfides, selenides, and tellurides). Unless the text indicates otherwise, the
term "metal chalcogenides" also includes "mixed-metal chalcogenides," implying more than one
metal element is included in the compound. The present invention can be practiced using any

1 suitable combination of metals and chalcogens, including both binary and multinary systems, and
including single- or mixed-metals and/or single- or mixed-chalcogens. Chalcogens in the present
description include the conventional chalcogen elements (S, Se, and Te), plus P and As. As will
be understood by those of skill in the art, a "single-metal" compound means a compound
containing only one type of metal; a "mixed-metal" compound means a compound containing
6 more than one type of metal. Similarly, a "single-chalcogenide" means a compound containing
only one type of chalcogen; a "mixed-chalcogenide" means a compound containing more than
one type of chalcogen. Thus, for example, the metal chalcogenide compounds of the present
invention may be expressed according to the following general formula:



11 where $M_1 M_2 \dots M_n$ is any combination of metals, and (P, As, S, Se, Te) is any combination of P,
As, S, Se, and/or Te.

16 The "chalcogenide salt" used in the methods of the present invention may be any
compound which contains a chalcogen (P, As, S, Se, or Te), and which reacts with a metal salt to
form a metal chalcogenide. As used herein, "chalcogenide salt" refers to a salt of the
chalcogenide anion which is partially soluble in the reaction medium, including, but not limited
to, alkali or alkaline-earth metal salts of the corresponding anion. Preferably, the salt contains a
metallic element of Group 1. In a particularly preferred embodiment, the salt contains sodium or
potassium. The metal salt and the chalcogenide salt are selected in such a manner that the
21 resulting metal chalcogenide is insoluble or slightly soluble in the reaction medium. Thus, any
metal salt and any chalcogenide salt which react to produce an insoluble or slightly soluble
chalcogenide product are useful reagents in accordance with the methods of the present
invention. It should also be understood that the metal salt(s) and the chalcogenide salt(s) used in
the methods of this invention may be applied as individual compounds and/or as mixtures
26 comprising two or more compounds.

For purposes of the specification and claims, the term "semiconductor nano crystals"
refers to quantum dots (nanometer-size semiconductor crystallites) each comprised of a core
comprised of at least one of a Group I-VII material, Group IV material, Group II-VI

1 semiconductor material (e.g., ZnS, and CdSe), a Group III-V semiconductor material (e.g. GaAs),
a III-VI material (e.g. InSe and InTe), a IV-VI material (e.g. SnS, SnSe, and SnTe), or a
combination thereof. In an additional embodiment, the semiconductor nano crystal may further
comprise a selected dopant (e.g., with a fluorescence property) such as a rare earth metal or a
transition metal, as known to those skilled in the art. The doping may be accomplished by using
6 a suitable chemical precursor containing the selected dopant, which is added in the solution
process. In a more preferred embodiment, the selected dopant is added in a proper amount for
doping during a stage of the process such as in the nucleation step or controlled crystalline
growth step so that the selected dopant is incorporated as part of, or embedded within, the crystal
lattice of the semiconductor core material.

11 Preferably, as selected from the aforementioned semiconductor materials, the
semiconductor nano crystal comprises a metal cation and an anion (e.g., the anion comprising a
chalcogenide when forming a Group II-VI material, or comprising a pnictide (phosphide or
arsenide) when forming a Group III-V material) which requires, in a formation process of
16 producing the semiconductor nano crystal, a mixing step, a nucleation step, and a controlled
growth step. In a more preferred embodiment, the semiconductor nano crystal comprises a metal
cation and the anion which requires, in a conversion process of producing the semiconductor
nano crystal, a mixing step, a nucleation step, a growth, a passivation or capping step, and a
drying/collecting step. It is possible that more than one temperature is used in the process (e.g.,
21 temperature at which nucleation occurs differs with the temperature of the growth termination
step or that of passivation).

26 For purposes of the specification and claims, by the term "particle size" is meant to refer
to a size defined by the average of the longest dimension of each particle as can be measured
using any conventional technique. Preferably, this is the average "diameter", as the
semiconductor nano crystals produced using the method according to the present invention are
generally spherical in shape. However, while preferably and generally spherical in shape,
irregularly shaped particles may also be produced using the method. In a most preferred
embodiment, the semiconductor nano crystals comprise a particle size in the range of

1 approximately 1 nanometer (nm) to approximately 20 nm in diameter.

6 The term "sol" refers to a two phase material system comprising the coordinating solvent (in combination with a carrier solution, if any, accompanying the starting materials), and the crystalline particles formed as a result of the organometallic reaction between the metal cation and the anion. In subsequent steps, the sol may further comprise semiconductor nano crystals formed as a result of the process. A sol, therefore, can include "colloidal nanocrystals" that are basically nano crystals dispersed in a liquid solvent.

11 For the purposes of simplifying the description of the method, material compositions of this invention will focus primarily on several selected compounds only; e.g. $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$, CdTe- and CdS-based structures. However, it should be understood that any metal or various combinations of metals including any ratio thereof, may be substituted for the Cu, In, Ga and Cd components and that P, As, S, Te, and Se or various combinations of P, As, S, Te, and Se may be substituted for the P, As, Se, Te and S components described in these methods and compositions, and that such substitutions are considered to be equivalents for purposes of this invention. Also, where several elements can be combined with or substituted for each other, such as In and Ga, or Se, Te and S, in the component to which this invention is related, it is not uncommon in this art to include in a set of parentheses those elements that can be combined or interchanged, such as (In,Ga) or (Se,Te,S). Doping can be used to introduce some dopants into nano-scaled semiconductor particles to change the electronic properties of these particles. Doping is well-known in the art. The descriptions in this specification sometimes use this convenience. Also for convenience, the elements are discussed with their commonly accepted chemical symbols, including copper (Cu), indium (In), gallium (Ga), cadmium (Cd), selenium (Se), sulfur (S), and the like.

26 The capping agent used in the practice of the present invention to passivate or protect the nucleated nano clusters is preferably a volatile capping agent. This volatile capping agent may be any capping agent (also sometimes referred to as a stabilizing agent) known in the art which is sufficiently volatile such that, instead of decomposing and introducing impurities into the

1 particles, it evolves during the powder formation step. As used herein, the term "volatile" is
defined as having a boiling point less than about 200°C at ambient pressure. The main purpose of
the capping agent is to prevent interaction and agglomeration of the nano particles, thereby
maintaining a uniform distribution of the colloidal substance (e.g., metal chalcogenide nano
6 particles), the disperse phase, throughout the dispersion medium. Volatile capping agents suitable
for use in the present invention are volatile compounds which contain at least one electron
pair-donor group or a group which can be converted into such an electron pair-donor group. The
electron pair-donor group can be electrically neutral or negative, and usually contains atoms such
and O, N or S. Electron pair-donor groups include, without limitation, primary, secondary or
11 tertiary amine groups or amide groups, nitrile groups, isonitrile groups, cyanate groups,
isocyanate groups, thiocyanate groups, isothiocyanate groups, azide groups, thiogroups, thiolate
groups, sulfide groups, sulfinates groups, sulfonate groups, phosphate groups, hydroxyl groups,
alcoholate groups, phenolate groups, carbonyl groups and carboxylate groups. Groups that can
be converted into an electron pair-donor group include, for example, carboxylic acid, carboxylic
16 acid anhydride, and glycidyl groups. Specific examples of suitable volatile capping agents
include, without limitation, ammonia, methyl amine, ethyl amine, acetonitrile, ethyl acetate,
methanol, ethanol, propanol, butanol, pyridine, ethane thiol, tetrahydrofuran, and diethyl ether.
Preferably, the volatile capping agent is methanol, acetonitrile, or pyridine.

21 The organic solvent (also herein referred to as dispersion medium or dispersing medium)
used in the present invention is not critical to the invention, and may be any organic solvent
known in the art, including, for example, alcohols, ethers, ether alcohols, esters, aliphatic and
cycloaliphatic hydrocarbons, and aromatic hydrocarbons. Specific examples of suitable organic
solvents include, without limitation, methanol, ethanol, propanol, butanol, diethyl ether, dibutyl
ether, tetrahydrofuran, butoxyethanol, ethyl acetate, pentane, hexane, cyclohexane, and toluene.
26 In a particularly preferred embodiment, the organic solvent is methanol.

In a preferred embodiment and to further illustrate the specifics of the present invention,
the method begins by mixing stoichiometric amounts of a metal salt with a chalcogenide salt in
an organic solvent to form a reacting fluid or "precursor fluid" and filling the pores of a nano-

1 porous polymer template with this precursor fluid. The reaction is permitted to proceed at
reduced temperature to precipitate a metal chalcogenide. The reaction conditions for the
above-discussed metathesis reaction are not critical to the invention. Thus, the reaction between
the metal salt and the chalcogenide salt can be conducted under moderate conditions, preferably
at or below room temperature and at atmospheric pressure. The reaction is typically complete
6 within a few seconds to several minutes.

11 In some cases, the reaction produces some by-product salts that must be removed or
separated from the desired quantum-sized material; e.g., NaCl or KCl produced in a metathesis
reaction. In these cases, the conversion of a "precursor fluid" is preferably performed outside the
pores of the template. Because of the large differences in solubility between the resulting metal
chalcogenide and the byproduct of the metathesis reaction, the two end products of this reaction
can be readily separated from one another using standard separation techniques. Such separation
techniques include, for example, sonication of the mixture, followed by centrifugation. The
soluble byproduct is then removed, for example, by decanting using a cannula, leaving an
16 isolated slurry of the metal chalcogenide. Volatile capping agent is then added to the isolated
metal chalcogenide to produce a non-aqueous mixture. Finally, the mixture is sonicated for a
period of time sufficient to facilitate "capping" of the nano particles by the capping agent, thereby
forming a stable, non-aqueous colloidal suspension of metal chalcogenide nano particles. These
colloidal nanocrystals are then introduced into the nano-pores of the template through pouring,
21 spraying, or dipping. The conversion step in this case involves essentially the removal of the
liquid solvent, allowing the nanocrystals to reside in the nano pores.

26 In one embodiment of the present invention, volatile capping agent is included in the
reaction mixture during nano particle synthesis. In this embodiment, stoichiometric amounts of
the metal and chalcogenide salts are reacted in the presence of the volatile capping agent at a
temperature and for a period of time sufficient to produce a nano particle precipitate. The
precipitate is separated from the soluble byproduct of the metathesis reaction, then mixed with
additional volatile capping agent to produce a non-aqueous mixture. This mixture is then
sonicated and centrifuged to produce a concentrated colloidal suspension. The concentrated

1 suspension is then diluted with additional volatile capping agent in an amount sufficient to
produce a colloidal suspension suitable for pore filling.

6 The passivating material can be selected from the group consisting of an organic
monomer, a low molecular weight polymer (oligomer), a metal, a non-metallic element, or a
combination thereof. The metallic element is preferably selected from Group IIB, IIIA, IVA, and
VA of the Periodic Table. The non-metallic element is preferably selected from the group
consisting of P, As, S, Se, Te, or a combination thereof. Another preferred class of passivating
materials contains phosphide, sulfide, arsenide, selenide, and telluride that is vaporized to deposit
as a thin coating on the compound semiconductor particles. The passivated semiconductor
11 particles not only have a higher tendency to remain isolated (not to agglomerate together), but
also have a higher quantum yield when used as a photoluminescent material. The latter
phenomenon is presumably due to a dramatic reduction in the surface electronic energy states
that would otherwise tend to result in a non-radiative electronic process.

16 For instance, passivation can be achieved by reaction of the surface atoms of the
quantum dots with organic passivating ligands, so as to eliminate the surface energy levels. The
CdSe nano crystallites can be capped with organic moieties such as tri-n-octyl phosphine (TOP)
and tri-n-octyl phosphine oxide (TOPO). Passivation of quantum dots can also be achieved by
using inorganic materials. Particles passivated with an inorganic coating are more robust than
organically passivated dots and have greater tolerance to processing conditions necessary for
21 their incorporation into devices. Examples of inorganically passivated quantum dot structures
are CdS-capped CdSe, CdSe-capped CdS, ZnS grown on CdS, ZnS on CdSe, CdSe on ZnS, and
ZnSe on CdSe.

26 The nano crystals trapped inside or bonded to the pore walls of a polymer template may
be collected by burning off the polymer walls to form a powder. The polymer walls may be
dissolved in a solvent and the resulting nano crystals are then dried and collected as a nano
powder 28 (FIG.1).

1 Alternatively, the polymer walls may be heated above the polymer melting point and then
allowed to re-solidify to remove or collapse any un-occupied porosity in the polymer, resulting in
a consolidated composite film 34 that is composed of nano particles dispersed in a polymer
matrix. Such a composite film is useful as a substrate material for opto-electronic device
applications.

6 The method may further include a step of removing the polymeric walls, such that a
plurality of voids 30 are formed in the quantum-sized material in positions which were
previously occupied by the polymeric walls prior to the removal of the polymeric walls. The
quantum-sized material on a solid substrate normally remained self-supporting after the polymer
walls were removed. The removal of polymer walls may be accomplished by immersing the
template in a polymeric wall-selective etchant or solvent. The method may further include the
step of refilling the voids with a supporting material to form a composite film 32. The
supporting material may be selected to have an index of refraction that is lower than that of the
quantum dots.

16 The following examples describe in detail the formation of selected semiconductor
quantum particles in accordance with preferred embodiments of the present invention:

21 EXAMPLE 1

In order to prepare cadmium telluride nano particles, a nearly stoichiometric ratio of
 $\text{Cd}(\text{CH}_3)_2$ (dimethylcadmium) in $(\text{n-C}_8\text{H}_{17})_3\text{P}$ (tri-n-octylphosphine or "TOP") and $(\text{n-C}_8\text{H}_{17})_3$
PTe (tri-n-octylphosphinetelluride or "TOPTe") in TOP were mixed together in a controlled-
atmosphere glove box to form a reacting solution. The solution was introduced into the nano
pores of a polystyrene template. The interstitial solution in the pores underwent precipitation of
CdTe nuclei (nucleation of nano clusters) in a liquid TOP solution. The liquid TOP solvent was
then evaporated, leaving behind nano particles in the pores.

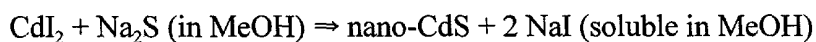
26 EXAMPLE 2.

The TOP-based reacting solution prepared in EXAMPLE 1 was mixed with liquified

1 (n-C₈H₁₇)₃ PO (tri-n-octylphosphine oxide or "TOPO") solvent maintained at the desired reaction
temperature from 54°C to about 125°C under N₂. The solution mixture was introduced into the
nano pores in a template to generate TOPO-capped CdTe particles. After a nominal reaction
period of from about one minute to about 60 minutes, in inverse relationship to the reaction
6 temperature, TOPO-capped cadmium telluride nano particles were precipitated. The resulting
film with a 2-D ordered array of CdTe crystals dispersed in a polystyrene matrix was washed
with methanol. The nano particles then were isolated and collected by dissolving the polymer in
benzene.

EXAMPLE 3

11 CdS nano particles were prepared by reacting CdI₂ in methanol with Na₂S in methanol at
reduced temperature under inert atmosphere as follows:



The by-product of the reaction (i.e., NaI) is soluble in the methanol solvent while the product
nano particles of CdS are not. During the chemical reaction, NaI salt is removed from the
product mixture with the remaining CdS nano particles forming a stable methanolic colloid. The
16 methanol colloid was poured into the pores of a nano-porous polystyrene template on a glass
surface. Methanol is then allowed to vaporize, leaving behind the CdS nano particles trapped
inside the nano pores. The polystyrene walls were melted at 130°C with the composite film
pressed between two glass slips, which was followed by re-solidifying the polymer to consolidate
21 the film.

EXAMPLE 4

A solution was prepared by dissolving a 0.002 mole of cadmium acetate in 200 ml of
ethanol at room temperature, which is followed by adding 0.002 mole of 3-aminopropyl-
26 triethoxysilane. Then, 0.005 mole of H₂S were added to the mixture and stirred at room
temperature for 10 minutes. The solution was poured onto a nano-porous polymer film wherein
nano-sized CdS clusters were precipitated. The liquid solvent was vaporized to produce the nano
crystals entrapped in the nano pores.

EXAMPLE 5

A solution was prepared by dissolving a 0.1 mole of zinc acetate in 260 ml of ethanol at 80°C, which was followed by adding 2 mole of 3-aminopropyltriethoxysilane. Then, 0.1 mole of H₂S was added to the mixture and stirred for 10 minutes. The solution is sprayed onto the surface of a polystyrene template. Nano clusters of ZnS were formed inside the nano pores. The solvent was removed, polystyrene was burned off, and resulting nano particles of ZnS were collected as a powder.

EXAMPLE 6

Samples of III-V compound semiconductor nano crystals were prepared through the following route: First, (NaK)₃E (E = P, As) was synthesized in situ under an argon atmosphere by combining sodium/potassium alloy with excess arsenic powder or excess white phosphorus in refluxing toluene. To this was added a GaX₃ (when E = As, X = Cl, I; when E = P, X = Cl) solution in diglyme. For the case of GaAs, the mixture was refluxed for 24 hours. The mixture solution was poured over the surface of a polymer template. The solvent was then removed. The resulting composite film was washed with deionized water, which was used to destroy any unreacted arsenide and to dissolve the alkali metal halide products. In the case of the GaP reactions, an ethanol/deionized water solution was used for the same purpose due to solubility of unreacted white phosphorus in ethanol. The resulting film was then vacuum treated and the solid film collected. The dry solid was heated to 350°C in a sublimator under dynamic vacuum for 2-3 hrs to remove excess Group V element. The resulting light to dark brown materials were GaAs and GaP nano crystals with approximate average particle size range from 6-22 nm as calculated from the X-ray diffraction patterns using the Scherrer equation.